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Depolymerization of PMMA-Based Dental Resin Scraps on Different Production Scales

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Abstract: This research explores the depolymerization of waste polymethyl methacrylate (PMMAW) from dental material in fixed bed semi-batch reactors, focusing on three production scales: laboratory, technical and pilot. The study investigates the thermal degradation mechanism and kinetics of PMMAW through thermogravimetric (TG) and differential scanning calorimetry (DSC) analyses, revealing a two-step degradation process. The heat flow during PMMAW decomposition is measured by DSC, providing essential parameters for designing pyrolysis processes. The results demonstrate the potential of DSC for energetic analysis and process design, with attention to standardization challenges. Material balance analysis across the production scales reveals a temperature gradient across the fixed bed negatively impacting liquid yield and methyl methacrylate (MMA) concentration. Reactor load and power load variables are introduced, demonstrating decreased temperature with increased process scale. The study identifies the influence of temperature on MMA concentration in the liquid fraction, emphasizing the importance of controlling temperature for efficient depolymerization. Furthermore, the research highlights the formation of aromatic hydrocarbons from the remaining char, indicating a shift in liquid composition during the depolymerization process. The study concludes that lower temperatures below 450 °C favor liquid fractions rich in MMA, suggesting the benefits of lower temperatures and slower heating rates in semi-batch depolymerization. The findings contribute to a novel approach for analyzing pyrolysis processes, emphasizing reactor design and economic considerations for recycling viability. Future research aims to refine and standardize the analysis and design protocols for pyrolysis and similar processes.

Keywords: PMMA waste; process design; thermogravimetry; differential scanning calorimetry; process scale influence

1. Introduction

The development and use of synthetic polymers for varied applications led to an increasing generation of plastic waste and environmental pollution [1]. Plastic use goes beyond availability and cost, since developed polymers excel in some applications, such as in the case of poly-methyl methacrylate (PMMA), an important polymer for transplants and prosthetics, especially in ophthalmology and dentistry fields, because of its biocompatibility, transparency, mechanical stability, aesthetic properties, absence of taste, and tooth adhesion [2–5]. Since PMMA is non-degradable, it is necessary to devise and apply an effective way to recycle this material (and other types of plastic) in order to avoid its accumulation in the environment and the pollution of terrestrial and marine ecosystems [6,7]. Plastic waste can be recycled through different strategies such as primary (reutilization of the almost unaltered waste for other applications), secondary (mechanical processes such as pelletizing, extrusion, injection molding, drawing and shredding), tertiary (chemical and thermochemical processes such as enzyme treatments, pyrolysis and gasification) and quaternary recycling (incineration). Of these strategies, one of the most promising for the recycling of PMMA is the pyrolysis process because research has shown that it is possible to obtain almost complete depolymerization of the PMMA chain, converting it to methyl methacrylate (MMA), its monomer of origin [1].

Primary recycling and secondary recycling of PMMA waste are not advisable due to its use in the medical field for implants and undesired properties for mechanical recycling such as thermal stability and hardness [2]. The incineration process reduces the volume of waste by combustion, recovering energy for other applications in the form of steam, displaying high investment and operational costs, as well as higher generation of pollutant gases such as CO₂ [1]. Pyrolysis involves heating the material in the absence of oxygen, causing it to thermally decompose into smaller, more volatile molecules, generating gaseous, liquid (bio-oil) and solid (char and coke) products; it is normally used in the production of charcoal from lignocellulosic material [8]. In the case of PMMA and polystyrene, the bio-oil composition is rich in their respective monomers (with few side products), which could be purified and repolymerized to create a “closed loop” in the PMMA industry, with reduced waste generation and value aggregation in its recycling chain [9]. From a process perspective, pyrolysis shows specific advantages such as reduced investment, lower operating costs, higher product value and simplicity of operation [1].

PMMA pyrolysis has been extensively studied by researchers worldwide [9–54]. From a process design perspective, some works can be highlighted for a better understanding of our study [9,14,20,40,52,53]. One essential question in process design is the difference between scales of production: What can be expected in the scale-up of a process? Kaminsky et al. [52] studied the scale-up of a mixed plastic pyrolysis plant utilizing a fluidized bed reactor and reported that homogeneous temperature distribution is easier to achieve in fluidized bed reactors, allowing a consistent product spectrum. They also reported that tire pyrolysis is not sensitive to the size of the input charge. They compared the product composition of polyethylene pyrolysis on laboratory (100 g/h) and pilot (20 kg/h) scales and observed higher production of methane, benzene and naphthalene for the pilot scale. They also tested tire pyrolysis in a fluidized bed reactor on the pilot and semi-industrial (120 kg/h) scale. The feed material of the semi-industrial scale was whole tires, and lower production of gaseous C₅ < hydrocarbons was observed, along with an increased concentration of higher-boiling-point aromatic compounds. Even though their work supplied a lot of information about the construction and details of the pyrolysis plants, no comparison was made regarding the influence of production scale on the yield of products [52].

Kaminsky et al. [14] studied PMMA pyrolysis in a fluidized bed for pure and aluminum trihydroxide (ATH)-filled PMMA on two scales of production: in a laboratory unit (3 kg/h) and in a pilot plant (16–34 kg/h). They concluded that for fluidized bed reactors, there is almost no difference in the scaling up of PMMA depolymerization, obtaining small differences in yields and MMA purity in both processing plants [14]. Table 1 shows filled

PMMA bio-oil yields of 94–96% and MMA purities of 87–90% in the laboratory unit and the yield of 93% and MMA content of 83% in the pilot unit. For pure samples, yields of 97–99% and MMA contents of 94–98% were observed in the lab, and a bio-oil yield of 98% and an MMA purity of 97% were observed in the pilot unit. They also reported that heat losses can be minimized in the pilot plant in a more efficient manner than in the laboratory unit [14]. Sasaki et al. [40] conducted experiments examining pure PMMA depolymerization in fluidized bed reactors on pilot (14.4 kg/h) and industrial (300 kg/h) scales and confirmed the small differences observed in the work of Kaminsky et al. [14], obtaining almost identical yields and MMA purities for both processing plants [40].

Table 1. Literature review of PMMA pyrolysis focusing on process scale.

References	PMMA Type	Temp. (°C)	Y _{LP} (%)	%MMA (wt.%)	Reactor Type	Process Scale
[9]	PMMA waste	345–420	48.2–55.5	83–98	Fixed bed	Pilot (143 L)
[10]	Filled PMMA	450	82.4	57.9	Fluidized bed	Lab (3 kg/h)
[11]	PMMA waste	490	92.1	91	Fluidized bed	Lab (3 kg/h)
[12]	PMMA waste	450	98.6	97.2	Fluidized bed	Lab (3 kg/h)
[14]	Filled and pure PMMA	450–480	94.7–96.2 (filled); 97.5–99.2 (pure)	86.6–90.5 (filled); 93.7–98.4 (pure)	Fluidized bed	Lab (3 kg/h)
[14]	Filled and pure PMMA	450	92.9 (filled); 98.3 (pure)	83.5 (filled); 96.7 (pure)	Fluidized bed	Pilot (16–34 kg/h)
[15]	Pure PMMA	450–590	57.3–98.5	95.8–98.7	Fluidized bed	Lab (2 g)
[16]	Pure and waste PMMA	440–500	98.1–99.3 (pure); 96.8–98.4 (waste)	96.3–97.4 (pure); 95.6–97.3 (waste)	Fluidized bed	Lab (1 kg/h)
[17]	Pure and commercial PMMA	450	99.3 (pure); 98.1 (commercial)	99.0 (pure); 96.8 (commercial)	Fixed bed	Lab (1.5 g)
[18]	Commercial PMMA	400–550	90.8–99.1	77.9–86.5	Conical spouted bed	Lab (1.5 g/min)
[20]	Pure and waste PMMA	250–450	9.0–85.0	82.2–99.9	Fixed bed	Lab (30 g)
[20]	Waste PMMA	400	66.3	76.4	Fixed bed	Lab (2 L)
[37]	Pure and waste PMMA	450	90–97	90.0–94.8	Fixed bed	Lab (20 g)
[38]	Filled PMMA	400–450	18–33	53–80	Fluidized bed	Lab (3 kg/h)
[40]	Pure PMMA	400	95	95	Fluidized bed	Pilot (14.4 kg/h)
[40]	Pure PMMA	400	95	94	Fluidized bed	Industrial (300 kg/h)
[48]	Filled PMMA	300–500	35–97	5–88	Fixed bed	Lab (50 g)

Braido et al. [20] studied waste PMMA from dental scraps in fixed bed reactors on two process scales: in a small borosilicate glass reactor (30 g of feed) and a larger stainless-steel reactor (2 L). They observed a liquid yield of 90% and an MMA content of 92.8% in the small lab unit in comparison to 66.3% and 76.4%, respectively, in the larger stainless-steel unit, confirming that mass and heat transfer are important for the conversion of PMMA into its monomer for fixed bed reactors [20].

The scale-up of PMMA pyrolysis plants is detailed in the work of Ding et al. [53], and they compared micro-scale (thermogravimetry) with bench-scale pyrolysis of PMMA in

a Fire Propagation Apparatus (FPA) in both experimental and simulation models. They observed the influence of particle size on the kinetics of PMMA depolymerization, where small particle size minimizes the physical mass and heat transfer process, and obtained accurate chemical reaction kinetics. Based on their experimental results, they concluded that it is difficult to scale up PMMA pyrolysis due to these effects. They also analyzed only the reaction kinetics, not the product yield or chemical composition [53].

In a previous study, dos Santos et al. [9] detailed the PMMA pyrolysis process in a semi-batch reactor on a pilot scale (reactor volume = 143 L), with a temperature range of 345–420 °C, and it was possible to obtain yields of bio-oil between 48 and 55% (wt.) containing over 90% (area) of the chromatogram of pure MMA. The material was fed in a relatively large particle size with average vertical and horizontal lengths of 5.94 and 8.69 mm, respectively, and an average weight of 100 mg [9]. These results suggest that PMMA depolymerization can be performed effectively in semi-batch reactors even with unoptimized mass and heat transfer conditions since these types of reactors are cheaper and easier to operate than a modern fluidized bed or conical spouted reactor [18,52]. Nevertheless, fixed bed reactors suffer from low throughput as the process is performed in batch mode, and high reactor volumes are needed to achieve the desired process throughput; assessing the influence of scale-up may be more important for these types of reactors. Table 1 summarizes some key aspects of the PMMA pyrolysis process detailed in multiple studies, such as PMMA type, temperature, liquid product yield (Y_{LP}), composition of MMA (%MMA), reactor type and process scale.

This work aims to evaluate the effect of process scale on the pyrolysis of PMMA dental scrap waste in fixed bed semi-batch reactors by analyzing the process in a small borosilicate lab unit (30 g), a stainless-steel reactor (2 L) and a pilot unit (143 L) and observing the effect on the product yields and MMA content in the liquid phase. The novelty of this work relies on the fact that PMMA depolymerization processes were never discussed from a scale-up point of view considering the geometry and equipment parameters associated with fixed bed reactors. First, the characterization of PMMA dental scrap waste (PMMAW) thermal decomposition was performed through thermogravimetry (TG/DTG) and differential scanning calorimetry (DSC). The process was evaluated through the measurement of process variables such as the temperature and reaction time; liquid fraction flow was recorded to observe the rate of production, and samples were fractionated according to reaction time. The liquid fraction was subjected to laboratory-scale fractional distillation in the range of 100–110 °C for further purification. Liquid composition was evaluated by gas chromatography coupled with mass spectrometry (GC-MS), and physical–chemical properties such as density and viscosity were measured for liquid and distilled samples.

2. Materials and Methods

Figure 1 illustrates the applied methodology used to analyze the PMMA depolymerization process in relation to process scale-up.

Dental scrap waste (PMMAW) was supplied by Dentsply Indústria e Comércio Ltda. (Petropolis, RJ-Brazil), and the formulation contained 1.0 wt% of titanium dioxide (TiO_2) and a crosslinking agent, 5.0 wt% of ethylene dimethacrylate (EGDMA). In order to predict its behavior in pyrolysis, the thermal decomposition of 5 mg of milled PMMAW was analyzed in a Shimadzu thermo analyzer (Kyoto, Japan, Model: DTG 60-H) in a temperature range of 25–600 °C, at a heating rate of 10 °C/min, under a nitrogen atmosphere (50 mL/min) in order to determine how temperature affects the weight loss of the sample. DSC was used to measure the energy flow during the thermal decomposition of the sample, and it was performed using a differential scanning calorimetry (NETZSCH-Gerätebau GmbH, Selb, German, Model: DSC 404 F1) under a nitrogen atmosphere (50 mL/min), in a temperature range of 25–500 °C, at a heating rate of 10 °C/min. A maximum temperature of 500 °C was used in DSC, and not 600 °C as in TG, because this is the highest temperature the equipment can achieve.

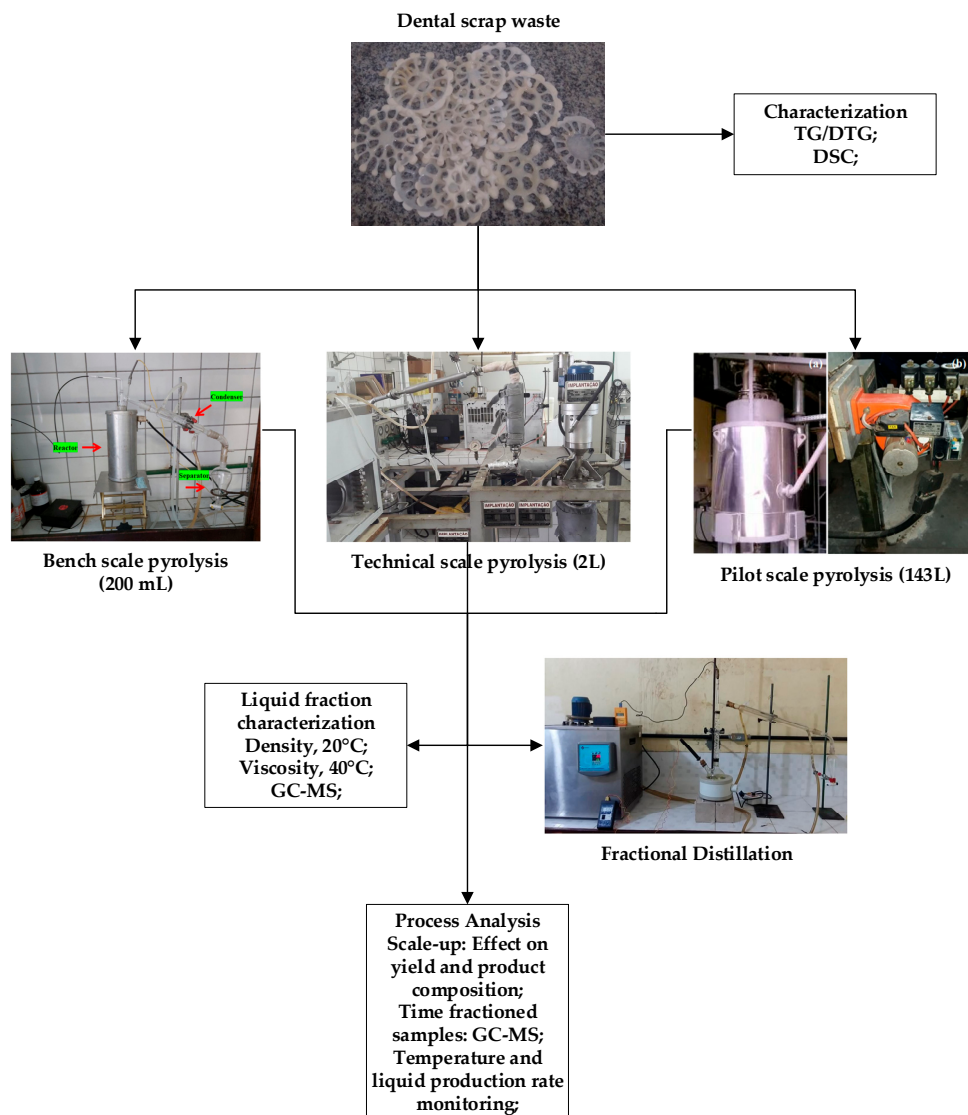


Figure 1. Research methodology applied to analyze process scale-up of PMMA fixed bed depolymerization.

All three fixed bed pyrolysis plants were accurately described in previous works [9,55–63]. Basically, the three reaction systems are constructed based on a classic semi-batch pyrolysis system (Figure 2) composed of a heated temperature-controlled fixed bed reactor coupled with a tube condenser operating with cooling water. The condensate and gases are separated in another vessel, where the liquid fraction is collected and the non-condensable gases produced are vented. The lab- and technical-scale reactors are heated by electrical heaters, of 800 W and 3500 W, respectively. The pilot unit is heated by an LPG gas burner (0–40 mbar, 5800–34,800 W). Since we are focusing on the process scale-up, it is important to mention the dimensions of the three reactors. Table 2 compiles the information about the internal diameter (i.d.) and height (h) of the three cylindrical reactors. A typical pyrolysis run uses a heating rate of 10 °C/min until the process temperature of 450 °C. The vapors and liquids formed were collected in the separating drum vessel, and the temperature was recorded every 10 min. After the reaction, the reactor was cooled naturally and opened so the formed char could be weighed. In the case of the technical and pilot scales, samples of liquid fraction were taken at each 10 min of reaction in order to evaluate process flow rate and variation in chemical composition with reaction time and process temperature.

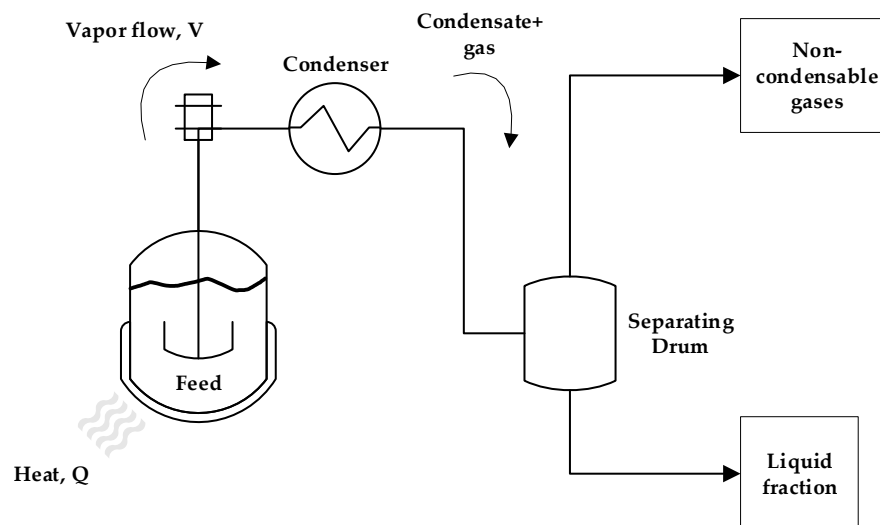


Figure 2. Classical setup of semi-batch fixed bed pyrolysis system.

Table 2. Dimensions of the three cylindrical reactors used to study the scale-up of PMMA depolymerization.

Reactor	i.d. (mm)	h (mm)	Volume (L)
Borosilicate glass	30	150	0.1
Technical	85	355	2.0
Pilot	300	1800	143

The liquid fractions of all three reaction systems were subjected to lab-scale ($V_{\text{sample}} = 250$ mL) fractional distillation in the boiling range of 100–105 °C in order to obtain purified MMA. Both the liquid fraction and distilled product were characterized according to standard procedures for density (ASTM D4052, 25 °C) [64], viscosity (ASTM D445/D446, 40 °C) [65], and refraction index (AOCS Cc 7–25) [66]. GC-MS analysis of the samples was performed to assess their chemical composition as described elsewhere [9]. Basically, 1 μ L of sample was dissolved in 1 mL of a combined solvent, acetone/toluene 50/50 *v/v*, and injected in split mode (1:50) into the GC equipment (Agilent, Santa Clara, CA, USA, GC-7890B, MS-5977A), with a capillary column of fused silica (SLB-5ms) (30 m $\times$ 0.25 mm), a film thickness of 0.25 μ m and helium as a carrier gas. The obtained mass spectra were compared to the NIST database, and composition is reported in TIC%. The detailed programming of the GC-MS is presented in Supplementary Materials Table S5.

3. Results

3.1. Thermal Decomposition and Characterization of PMMA Dental Scraps (PMMAW)

PMMAW was characterized by TG/DTG with respect to the weight loss of the sample and DTA and DSC analysis to evaluate the heat flow during the depolymerization process. Thermogravimetry provides useful information when designing pyrolysis or depolymerization processes, for all types of reactors and modes of operation. The small sample size allows a uniform distribution of temperature on the feed material and minimizes the effects of deficient mass and heat transfer due to the particle size, bed thickness and thermal conductivity of the material being analyzed [47]. TG/DTG analyses provide information about the number of stages of decomposition of a sample together with peak temperatures (temperature of maximum decomposition), suggesting the reaction order and kinetics of sample decomposition. The TG/DTG results are shown in Figure 3, highlighting the main stage and peak temperature of the decomposition of PMMAW. The results show a single decomposition stage beginning at 327 °C and ending at 405 °C with a peak at 366 °C. The decomposition kinetics of PMMA samples is affected by parameters such as temperature and the molecular weight of the polymer, which change the thermal decomposition of

PMMA polymer and present different reaction mechanisms [15]. Barlow et al. studied PMMA degradation kinetics and mechanisms in the temperature range of 340–460 °C using a micropyrolysis technique (Py-GLC) for PMMA polymers of different molecular weights (MW = 64,850–579,500 g/mol) and observed that the decomposition reaction can be separated into two different initiation steps and two termination steps, forming four different possible reaction sequences. The initiation steps are classified depending on the type of initiation, i.e., chain-end or random scission initiation, as shown in Equations (1) and (2). P is the PMMA polymer, $R\cdot$ is the chain radical that will depropagate and $X\cdot$ is a small radical that distills out of the system.

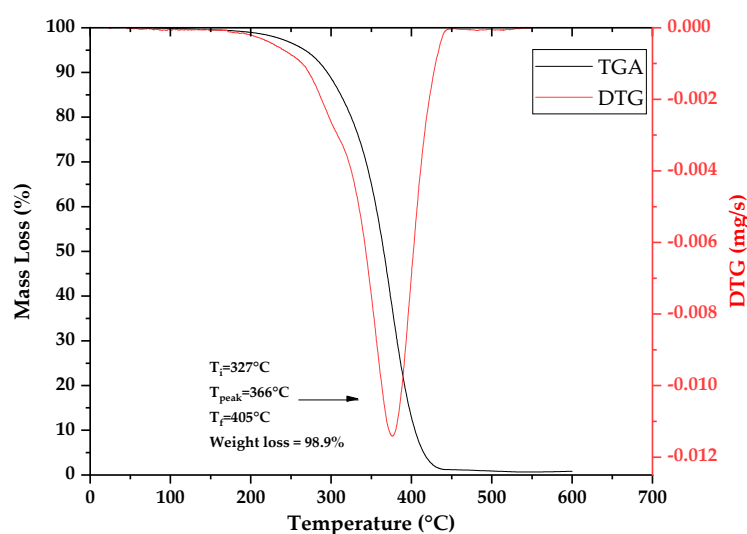
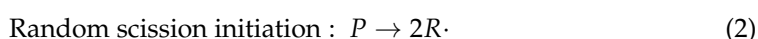
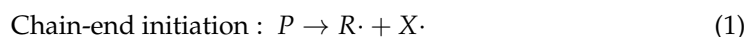
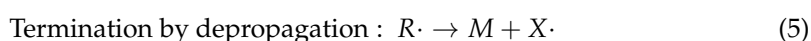


Figure 3. TG/DTG measurement of PMMAW.

The next step is the classical depropagation of the chain radical, producing another radical and the monomer MMA, which distills out of the system, and it is common to all reaction mechanisms. As most works show, MMA is the main compound obtained from PMMA pyrolysis, and this step governs the overall reaction rate and is represented by Equation (3).



The termination step differs; here, the reaction could follow termination by bimolecular interaction or termination by depropagation until the end of the polymer chain, as Equations (4) and (5), respectively.



At low temperatures, below 340 °C, the observed reaction mechanism is governed by Equations (1), (3) and (4), exhibiting chain-end initiation and termination by bimolecular interaction. In this case, low conversions should be achieved with substantial formation of char and gases. As temperature increases, the reaction tends to exhibit random scission initiation and depropagation to the end of the polymer chain, as shown in Equations (2), (3) and (5), producing a high yield of the liquid phase and a low yield of char and gases in PMMA pyrolysis [67].

Several authors studied PMMA degradation by TG/DTG and agree that the decomposition of some solid PMMA samples can be adequately represented by a single stage in inert atmospheres of nitrogen and argon depending on the molecular weight of the polymer, the temperature, and the type and agents of polymerization [9,13,15,16,18–20,22–24,47]. Peterson et al. [24] observed that a small first step of decomposition occurs at vinylidene end-groups, but this step usually overlaps with the following step of degradation by random scission, especially at higher heating rates [24]. In fact, it can be seen in Figure 3 that weight loss starts to occur as early as 200 °C at a slow rate, increasing with temperature until 361 °C. Nevertheless, DTG only shows a single peak of decomposition, possibly due to the use of 10 °C/min as the heating rate, making it impossible to distinguish between the two peaks of decomposition. Da Ros et al. [47] proposed a three-step degradation mechanism for the thermal decomposition of EGDMA-crosslinked PMMA waste but suggested that a two-step consecutive reaction and single-stage decomposition could also represent the more thermally stable sample of the crosslinked polymer. Homopolymer PMMA exhibited earlier degradation at 150 °C and more pronounced peaks in the DTG analysis [47]. Manring et al. [23,35] suggested that different end-groups may be associated with different thermal behaviors and pointed out that vinyl-terminated PMMA degraded at lower temperatures because of the unsaturated end-group, generating a radical unzipping of the polymer chains via a chain transfer process, and that unsaturated bonds formed by termination in the polymerization process are unstable at the ends of polymer chains. They also commented on the fact that thermal degradation behavior differs depending on the polymerization agent used [23,35]. These observations are also present in the work of Hu et al. [25], who studied the effects of end-groups in the thermal decomposition of PMMA [25].

The assumption of a single-step reaction and first-order kinetics for PMMA thermal degradation is reasonable due to the magnitude of the depropagation step forming the MMA monomer, and several authors successfully modeled PMMA degradation in this manner [13,27,32,54,67]. Gao et al. suggested that the different authors identified multi-step degradation due to the presence of weak links in the PMMA polymer intensifying the initial degradation steps and showing more than one peak in DTG [27]. Since most of the product of PMMA pyrolysis is MMA, it is natural to assume that the depropagation step suggested in Equation (3) governs the overall reaction rate. Even when considering all the other steps, the reaction can still be represented by first-order kinetics with a modification of its reaction rate constant [67]. The limitations of this assumption would be some uncertainty due to added error in calculated values like temperature, reaction rate constants and conversion, but as the liquid product is almost exclusively formed by MMA, this error should be minimal.

Hu et al. [25] conducted several TGA experiments on PMMA samples prepared using different polymerization agents in order to elucidate the thermal degradation mechanism and the “blocking effect” of different end-groups since the initial temperature of degradation of PMMA seems to be affected by the type of end-group present. The type of end-group depends upon the polymerization agent, so it is possible to increase the thermal stability of the PMMA polymers, which degrade only at higher temperatures. These authors observed that polymerized PMMA initiated with 2,2'-azobisisobutyronitrile (AIBN) presented two stages of weight loss (corroborated by DTG), one of them at low temperatures between 200 and 300 °C and the other, more intense, between 320 and 400 °C. This first peak was not observed for PMMA polymerized using thiols, where the end-group contains specific units such as $-S-(CH_2)_{11}-CH_3$, $-S-(CH_2)_2-COOH$ and $-S-(CH_2)_2-OH$, and thermal degradation occurred only at temperatures higher than 300 °C via main-chain scission, blocking the unzipping via the end unit, particularly at low temperatures [25]. The TGA for PMMAW in this work presented low-temperature degradation but not as intense as that observed for PMMA-AIBN in the work of Hu et al. [25], as shown by the single peak in DTG, indicating that the blocking effect can be augmented or suppressed by other mechanisms or parameters.

It is worth noting that considerable variability exists in the thermal decomposition of PMMA, even with rigorous TG procedures, and this was pointed out by several authors [22,24]. As was observed earlier, the degradation of the polymer chain may occur through different mechanisms, influenced by the temperature, molecular weight and polymerization agent. Furthermore, the thermal degradation of PMMA is usually performed in the solid phase, and heterogeneous reaction rates are influenced by mass and heat transfer processes. Even though thermogravimetry usually needs low weights (in the order of mg) of ground samples, minimizing mass and heat transfer, some influence is inevitably present, especially in the case of long polymeric chains [9,13,15,16,18–20,22–24,47].

The presence of a crosslinking agent also influences the mechanism of PMMA degradation. PMMAW contains 5.0 wt% of EGDMA as a crosslinking agent, the effects of which were studied by Bate and Lehrle [54] and Braido et al. [20,47]. A study on the kinetics of the thermal degradation of crosslinked PMMA using a heated filament, with Py-GC/MS analysis, concluded that presence of EGDMA as crosslinking agent exerts a blocking effect on the unzipping of the polymeric chain, showing lower reaction rates when compared to non-crosslinked PMMA even though they initiate by the same mechanism, but the unzipping seems to be stabilized when it reaches a crosslinking unit [54]. Indeed, Braido et al. [20,47] used TGA to compare the thermal degradation of homopolymer PMMA with that of EGDMA-crosslinked PMMA waste and concluded the homopolymer starts to degrade at lower temperatures, as early as 150 °C, while the crosslinked sample started to degrade at temperatures of 200 °C with a lower rate of mass loss. The PMMAW in this work presented a similar behavior to what was observed for the crosslinked samples of the other authors, showing that crosslinked PMMA is more thermally stable than the pure polymer [20,47,54].

The energetic characterization of the thermal degradation of PMMAW was performed by DSC, as displayed in Figure 4. Differential scanning calorimetry is a thermal analysis technique where the sample and a reference (normally the empty furnace) are heated on a double furnace. The heat flow is controlled in a feedback loop in order to maintain an equal temperature between the sample and the reference, and it is used to compute useful thermodynamic parameters such as the heat capacity of the sample and the energy traded in physical transformations and chemical reactions [46]. It is commonly used to study material properties such as glass transition temperatures and heats of fusion and for the general calculation of reaction enthalpy [68]. The use of the DSC technique to study pyrolysis or gasification processes is not that widespread, mainly because the calculations are performed based on the initial weight of the sample, and in thermal decomposition processes, there is considerable variation in this weight as the feed pyrolyzes into gases. Some authors circumvented this problem by considering the mass available at each heat flow peak in simultaneous TG/DSC equipment [69,70]. In order to accurately measure the energy involved in chemical reactions, one must integrate the signal of heat flow $\times$ time (peak area) for each detected reaction peak, and since there is variation in heat capacity with temperature, the detection of some peaks is not so direct, and often, if not always, baseline correction (extraction of heat capacity variation from the curve) is needed to accurately define a peak and integrate its area [70]. Even then, the results have to be closely observed since multiple transformations can be coupled in a single peak, making its analysis difficult.

Varied strategies can be used to extract heat capacity from a DSC curve. Chen et al. [66] determined the heat of biomass (wood) pyrolysis by simultaneous TG/DSC estimation of specific heat capacity using a weighted average of heat capacities from the sample and leftover char in the reactor [69]. Other mathematical methods involve graphically fitting functions representing the heat capacity and subtracting them from the DSC curve. A combination of functions can be used when the baseline is sufficiently complex. Figure 5 shows the baseline-corrected DSC curve of PMMAW pyrolysis, produced in Origin 2018 Software by subtracting the baseline using a spline function.

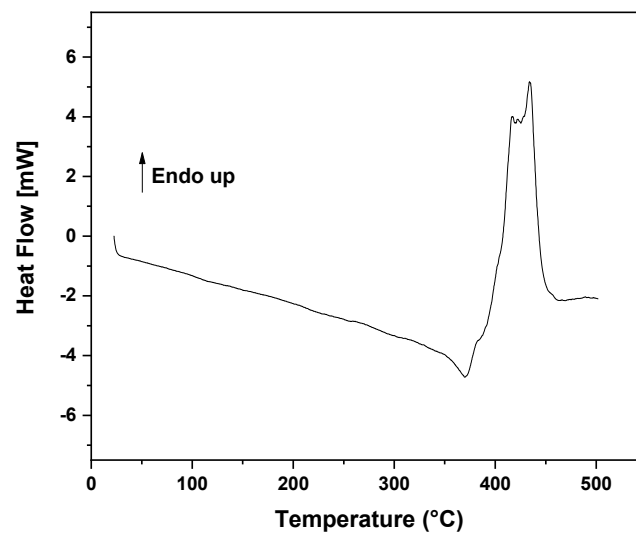


Figure 4. Heat flow measured by DSC of PMMAW at heating rate of 10 °C/min and under nitrogen atmosphere.

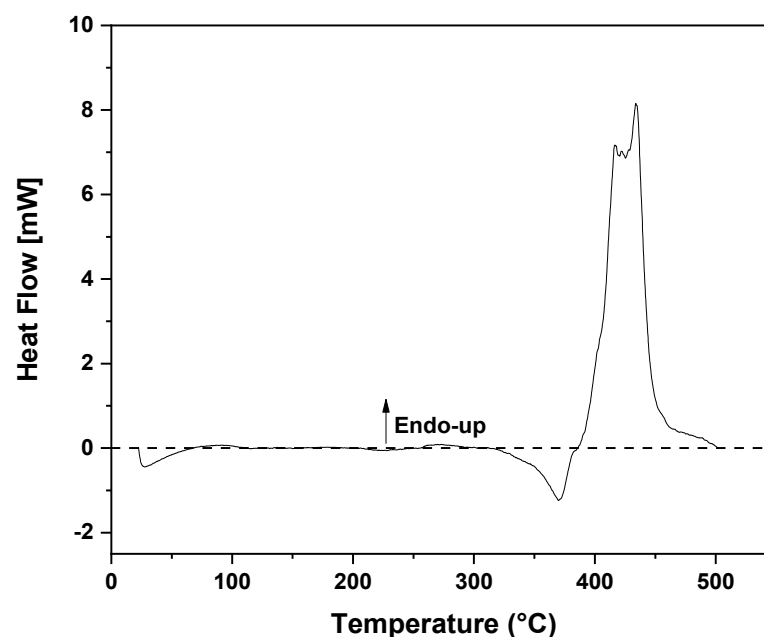


Figure 5. Baseline-corrected (heat capacity extraction) heat flow measurement of PMMAW decomposition.

An analysis of Figure 5 reveals the presence of one large endothermic peak between 370 and 433 °C. It is difficult to accurately describe energy trades in pyrolysis such as the heat of pyrolysis and vaporization enthalpies of products since many processes are coupled and happening at the same time. The actual value of heat of pyrolysis depends heavily on the feedstocks, temperature ranges, the heating rate, the extent of secondary reactions and even measurement conditions, and the accurate determination of this value is challenging. There are inconsistent results in the literature, ranging from overall endothermic to exothermic [71]. A literature review of DSC applied to PMMA for the energetic characterization of its thermal decomposition presents mixed results for its thermal decomposition. Most studies focused on transitions below 200 °C, such as glass transition temperatures for composites prepared using PMMA and other plastics [68,72–77], or assessed the mechanical and thermal properties of the polymer [78–80]. Reports of DSC analysis of the thermal decomposition of PMMA performed under higher temperature conditions are

scarce [81–83]. Fiola et al. [81] analyzed the thermal properties of extruded and cast PMMA by DSC, finding an endothermic peak between 327 and 427 °C for both samples with values of integrated heat flow (measure of the process enthalpy) of 1.5 J/g [81]. Wang et al. [83] tested PMMA composites through DSC under a nitrogen atmosphere and different heating rates (10–30 °C/min) and found three stages of decomposition with three endothermic peaks [83]. Alonso et al. [82] used DSC to analyze the thermal decomposition of PMMA under different mass quantities and different atmospheres, observing endothermic peaks in a nitrogen atmosphere [82].

An accurate determination of the energy involved in each transition corresponding to individual peaks can be difficult, and by observing Figure 5, one could make the assumption that there exists more than one peak in the decomposition of PMMAW, including one previous exothermic step and a later third endothermic stage. Analysis by a single-step mechanism was an initial assumption made based on academic literature [9,13,15,16,18–20,22–24,47] and to keep its description simple and general in order to be applied to other feedstocks, even though it is possible to describe the thermal degradation of PMMA in more than one step [20,47]. DSC has quantitative capabilities, but they are better applied to well-known processes and reactions where knowledge of the actual mechanism involved is modeled in the calculations, including equipment-specific parameters such as neutral baseline (heat flow difference between an empty pan and the reference). Baseline correction can also be performed by using a modeled equation of $c_p \times T$ and considering the heat capacity of the remaining char [81]. For pyrolysis reactions, the weight of the sample changes as the vapors flow out of the system, and a correction is needed for the calculation of the energy of individual peaks [71].

In the thermal decomposition of PMMA, there are some simplifications and complications associated with the calculation of the related energy of individual DSC peaks. PMMA decomposition stages can be approximated to a single step as shown by the DTG curve in Figure 3, and practically no char is generated, so no correction is needed for the variation in weight of the sample. Since no char is generated, the influence of char heat capacity on the DSC curve is minimal. The product of PMMA depolymerization is mainly MMA, largely simplifying the analysis of thermodynamic parameters.

Complications arise when considering the processes involved in the thermal decomposition of PMMA, mainly because of specifics related to the actual structure of the polymer such as the presence of crosslinking agents, end-groups and the degree of polymerization (molecular weight of the polymer), generating a large variation in values of known thermodynamic quantities such as the heat of decomposition of the sample and making the DSC energetic analysis model-specific. Nevertheless, the integration of the endothermic peak generated values of 423 J/g with an integral heat (entire energy used, including heating the sample, frequently called heat of gasification) of 1748 J/g. This peak seems related to the vaporization enthalpy of MMA of 40.1 KJ/mol or 401 J/g, but higher quantities were expected since the heat of depolymerization of PMMA should be in the range of 560 J/g. Indeed, the reported decomposition heat of PMMA is in the range of 820 J/g [81]. The heat of gasification obtained in PMMAW DSC is in accord with other numbers reported for the thermal decomposition of PMMA [81–83].

DSC presents an interesting analysis for the quantification of energy trades and reactions involved in PMMA pyrolysis and possibly other pyrolysis processes as well, but some improvements must be made to accurately characterize and quantify the energy of each specific step. First, it is better to conduct simultaneous TG and DSC analysis for accurate quantification of sample weight in each energy peak. Second, the calibration should be performed with pyrolysis of a known sample for an accurate conversion of the signal (mW) into specific energy values (J/g or J/mol). Third, accurate knowledge of the reaction steps involved should be used in order to predict and measure the energy involved.

3.2. Process Analysis

3.2.1. Scaling-Up Effect on the Yield of Products

The process conditions and yields of products obtained for the three scales of production are summarized in Table 3. It can be observed that very different liquid yields are achieved when comparing the laboratory scale and the other two scales of production. Liquid yields tend to decrease with an increase in the volume of the reactor. As discussed earlier, in order for PMMA decomposition to occur in a single reaction step, with a small production of side products, and produce a consistent liquid composition, a higher mass and heat transfer is necessary, allowing the reaction to proceed with a uniform temperature across all sections of the reactor, a condition observed in the case of fluidized bed reactors [14,40]. In the case of unstirred fixed bed reactors loaded with solid feed, such as PMMAW, there is a temperature gradient from the external wall of the tube reactors to their center (bulk temperature). In the case of the small glass reactor, the distance from the wall to the center is only 15 mm, and the temperature gradient is small. This is shown by the difference in the temperature of initial condensation of products in the three reactors: while technical and pilot depolymerization condensed products at temperatures of 109 and 113 °C, respectively, the laboratory experiments displayed an initial condensation temperature of 230 °C. This effect can be further amplified or minimized by material type and particle size, since the heat conductivity, particle size and packing of the bed all influence the mass and heat transfer occurring during the depolymerization reaction. The char shape obtained in the experiments was very reminiscent of the original material, and DSC analysis (Figure 4) did not show a characteristic change in heat capacity indicating melting of the sample, suggesting that the material remained in its original shape during pyrolysis.

Table 3. Process conditions and yields of reaction products for thermal degradation of PMMA-based dental resin fragments/residues at 450 °C, atmospheric pressure, on laboratory, technical and pilot scales.

Process Condition	Temperature [°C]		
	450		
	Laboratory	Semi-Pilot	Pilot
Mass of feed [g]	40.00	625.00	20,000
Reactor volume [L]	0.1	2.0	143
Reactor load [kg/L]	0.40	0.31	0.14
Power load [W/kg]	20,000	5600	290–1740
Reaction time [min]	60	100	130
Temperature of liquid condensation [°C]	230	109	113
Final temperature [°C]	450	455	458
Mass of coke [g]	0.29	15.11	1700
Mass of liquid [g]	38.31	384.70	11,836.3
Mass of gas [g]	1.46	223.94	6463.7
Yield of liquid [%]	95.63	61.67	59.18
Yield of coke [%]	3.64	2.43	8.50
Yield of gas [%]	0.73	35.90	32.32

Two variables have been defined to assist in understanding our analysis, reactor load (kg/L) and power load (W/kg). The reactor load is the ratio of the weight of PMMAW to the volume of the reactor and is a measure of the occupation of the fixed bed, while the power load is defined as the ratio of available heating power to the weight of feed in the reactor. It can be observed that the reactor load decreased with the scale-up, meaning that for larger volumes (technical and pilot), the feed occupied a smaller portion of the fixed bed.

This should minimize the temperature gradient to the center of the fixed bed, but it can be observed that the power load still decreases with scale-up and the reaction takes more time on technical and pilot scales. This decrease in power load associated with the larger volume of feed in the three reactors and the low thermal conductivity of the PMMAW bed further increased the temperature gradient to the center of reactor, so while the bulk temperature on technical and pilot scales reached values of 450 °C, it is probable that higher values were achieved near the wall of the reactor, increasing cracking of molecules and gas formation. The power load of 20,000 W/kg in the laboratory unit is sufficient to achieve a uniform temperature across the fixed bed of feed, making it easier to control the reaction with better temperature control. It is important to mention that the power load only considers the available power supplied by the equipment, not the actual power used in the experiment. The results showed that lower reactor loads associated with higher power loads increase the amount of gas formed probably due to an increase in the temperature gradient across the fixed bed radius. Temperature increases in fixed bed pyrolysis have been shown to affect negatively liquid yield and MMA concentration in pyrolysis oil due to side reactions influenced by higher temperatures [9], as shown in Figure 6, which displays the influence of temperature on product yields for the technical scale. From 425 to 450 °C, liquid yields decreased from 82 to 61 wt.%, indicating that temperature largely influences the yields of products. Unlike on the technical and pilot scales, the reactor temperature thermocouple was situated outside of the reactor, and actual reactor temperatures were possibly lower, while for the technical and pilot scales, the thermocouple is situated in the center of the fixed bed, and temperatures at the edges of the reactors are higher than the setpoint of 450 °C, augmenting the production of side products in liquid and gaseous phases. The slower heating rates in the larger fixed bed of PMMAW also increased char yields with process scale, corroborating what is observed in academic literature for many types of materials [55–57].

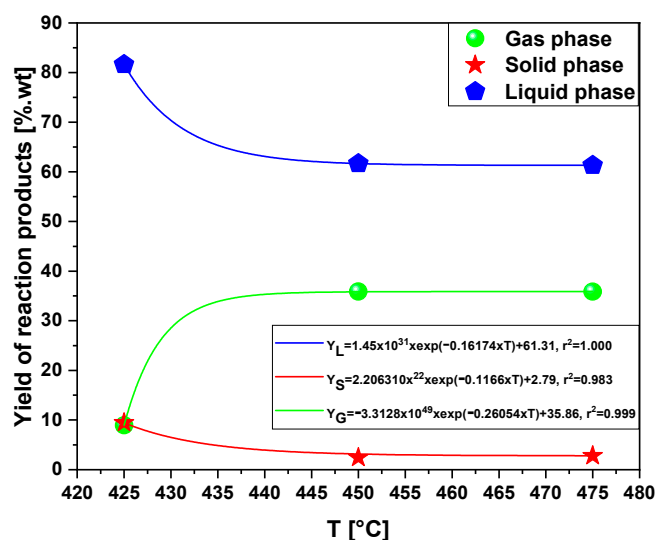


Figure 6. The effect of temperature on the yield of liquid, coke and gas-phase products in the depolymerization of PMMA-based dental scraps at 425, 450 and 475 °C on the technical scale.

Since pyrolysis process products are influenced by temperature and heating rates, it can be concluded that the characteristics of the feed such as specific heat, thermal conductivity and particle size and the characteristics of the process such as reactor geometry, heating mode and residence time are connected to temperature effects, influencing the yields of products. This is especially true for fixed bed reactors, where large vessels tend to show far more temperature differences across the fixed bed geometry packed inside the reactor. As detailed in Section 3.2.2, it seems that temperatures below 425 °C tend to

produce the highest amount of the liquid phase and the highest content of MMA, at least for fixed bed semi-batch reactors.

In semi-batch pyrolysis, where vapors flow continually out of the heated reaction zone by cracking and vaporization (endothermic processes), the reaction temperature tends to stay in specific ranges determined by reaction kinetics and present substances, and the heat supplied by the electrical heater is consumed in the process of physical or chemical transformations. For larger reactors, almost no difference is observed in the reactor thermocouple until the endothermic processes complete, in this case, the depolymerization reaction of PMMAW and subsequent vaporization of products. As its thermal decomposition of PMMAW occurs around 150–200 °C and the main product from the depolymerization of PMMAW is MMA, with a boiling point of 101 °C, the reactor temperature tends to remain in the 200 °C range for larger vessels. This can be seen in the graph shown in Figure 7, which displays the reactor temperature profile of the pilot reactor and recovered liquid phase as a percentage of the total liquid phase obtained. More than 93 wt.% of the liquid phase collected was produced between 145 and 208 °C. Only a small percentage of the liquid phase was collected at higher temperatures. It can be observed that the vapor flow production halted the reactor heating, producing an inflection at 40 min of reaction time, and the reactor temperature changed little. After almost all the liquid had vaporized, the temperature started rising again to the desired setpoint. Nevertheless, different process temperatures of PMMAW depolymerization (425–475 °C) were tested in the technical plant, and considerable differences were observed. First, liquid yields were far higher for 425 °C, reaching values of 81.6%, whereas for 450 and 475 °C, they reached 61% (Figure 6). As detailed in Section 3.2.2, MMA concentration also varied with temperature, decreasing with increasing temperature, revealing that even though it is not possible to choose a desired reaction temperature (defined by process thermodynamics), it is possible to obtain different heating rates that largely influence product yields and quality.

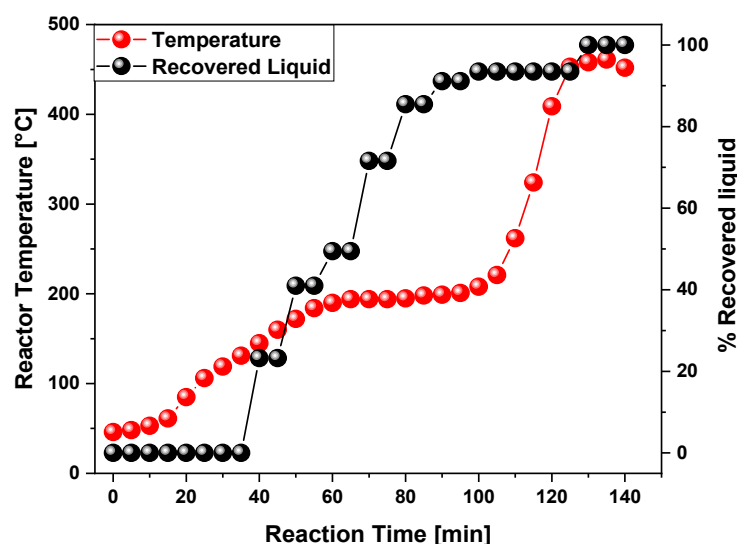


Figure 7. Pilot reactor temperature and % recovered liquid phase profile of PMMAW depolymerization at 450 °C.

It is interesting to note that this temperature behavior is only present for the larger vessels: the technical and pilot plants. For the laboratory scale, the thermocouple is positioned outside of the reactor and there is a considerable power load (20,000 W/kg), meaning that temperature gradients across the geometry of the fixed bed are low. Figure 8 compares the temperature profiles of the three production scales and shows that pyrolysis took place between 193 and 369 °C, similar to what is presented in the TG analysis (Figure 3). The adjustment and control of temperature in semi-batch reactors is related to the amount of power supplied and the quantity of feed in the reactor. For low power loads, where it is

not possible to adjust reactor temperature beyond a certain point, the process temperature represents the extent of the reaction and the heating rate applied. For higher power loads, it is possible to improve the reaction temperature, and for PMMAW, this means a higher yield of the liquid phase associated with a higher concentration of MMA due to the minimization of temperature gradients across the fixed bed.

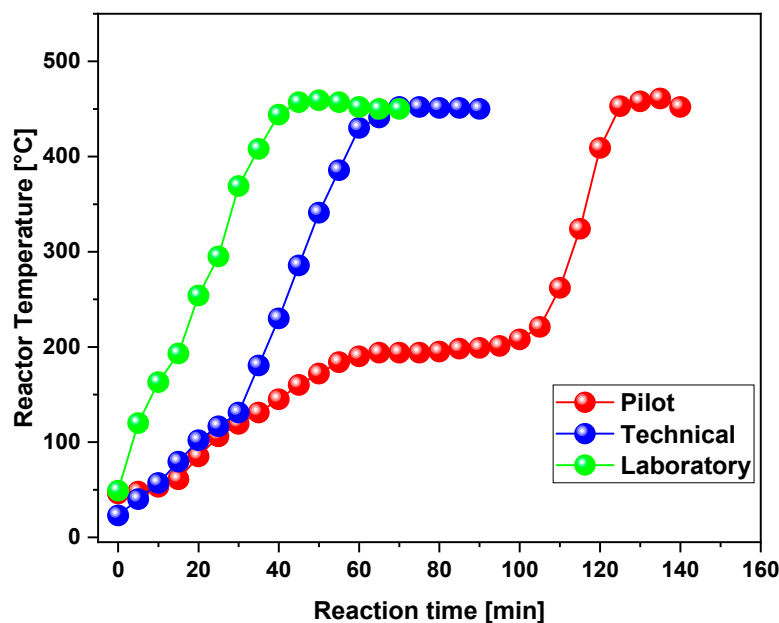


Figure 8. Temperature profile ($T \times t$) of PMMAW depolymerization process on laboratory, technical and pilot process scales.

The temperature profile of the larger vessels is similar until 50% of the recovered liquid is collected, corresponding to 40 min of reaction time. As shown in Figure 9, PMMAW depolymerization on the technical scale occurred between 102 and 430 °C, with more than 50% of the recovered liquid being collected before temperatures of 250 °C were reached. From that point, the power load of the technical plant allowed a linear increase in temperature, while more liquid was collected. As detailed in Section 3.2.2, it is clear that the liquid phase was 100% MMA until 40 min of reaction time and afterward slowly changed to other compounds such as methyl isobutyrate and aromatic hydrocarbons (benzene, toluene, xylene and others). This suggests that for lower power loads, in order to maximize MMA concentration, there is a need for lower temperatures, which minimize the formation of side products. Lower power loads mean effective lower heating rates for parts of the PMMAW fixed bed, allowing the formation of more char and stopping the unzipping of the polymeric chain, reducing the formation of MMA. In fact, on the technical and pilot scales, where the formation of char is significative (higher than 5%), the chemical composition of vapors and the liquid fraction changes from MMA to chemical compounds normally encountered in the pyrolysis of coal, such as aromatic hydrocarbons [84]. For the laboratory scale, with a high power load, almost all the material reaches the same temperature, and the reaction is allowed to occur in a few minutes (20 min); the formation of char is minimized, and the liquid fraction collected is almost exclusively formed by MMA.

These observations are corroborated by the reaction mechanism presented in Section 3.1. For low temperatures, the reaction is initiated at the ends of the chain, depropagates to form MMA and is terminated by a bimolecular interaction, forming an intermediate polymer that transforms into char via aromatization and carbonization reactions. This can be observed on the technical and pilot scales, where the reactions were conducted using lower power loads than the laboratory scale and lower liquid yields (~60%), higher gas yields (~30%) and higher amounts of char (5–8%) were obtained in comparison to the lab scale, where

liquid yields of over 95% were obtained. As was discussed, the presence of a temperature gradient between the rim of the fixed bed and its center indicates that much of the reaction took place in low temperatures, favoring the reaction mechanism of bimolecular interaction and forming more gases and char. In the laboratory unit, where there is a power load of 20,000 W/kg and the dimensions of the feed inside the reactor are almost negligible when compared to the heat supplied, there is no temperature gradient, and the degradation mechanism is much like the one presented in TG analysis (Figure 3) where the reaction is dominated by a single peak of decomposition representing an initiation step by random scission and termination by depropagation of a radical to the MMA monomer until end of the polymeric chain. This is corroborated by the high liquid yield and MMA concentration of laboratory-scale pyrolysis oil.

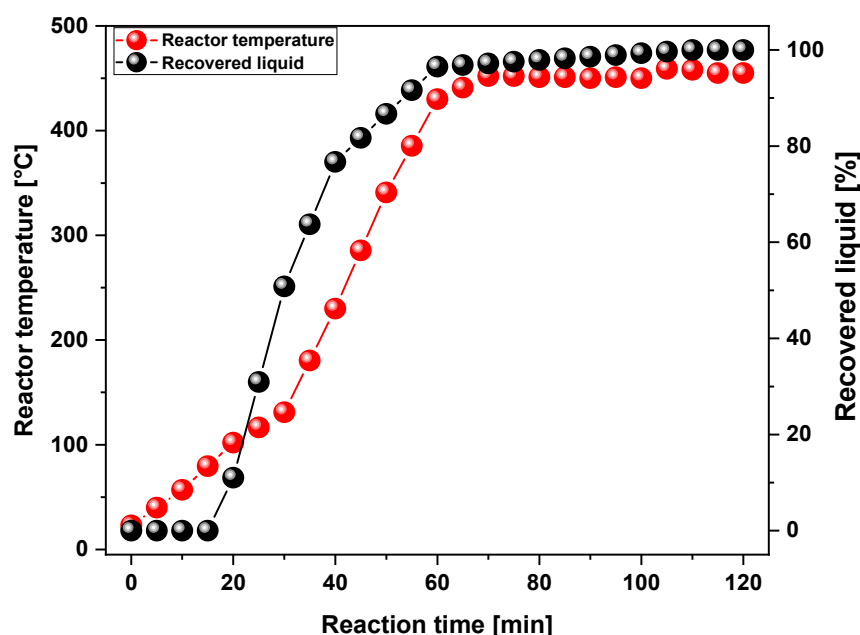


Figure 9. Technical-scale reactor temperature and % recovered liquid phase profile of PMMAW depolymerization at 450 °C.

3.2.2. Scaling-Up Effect on the Chemical Composition of the Liquid Phase

The effect of an increase in the production scale on the concentration of MMA in the liquid phase, as shown in Figure 10, can be analyzed as a function of reaction time. The weighted average of the MMA concentration in the liquid phase (considering the weight of each time-fractionated sample) is shown in the graph along with the obtained MMA concentration of liquid bio-oil from the laboratory scale, since the initial low feed weight made it impractical to divide laboratory bio-oil according to reaction time. The detailed chemical composition of all samples is supplied in Tables S1–S5 as Supplementary Materials.

Both curves of MMA concentration in the technical and pilot plants show similar behavior with respect to reaction time, maintaining values near purity (>90 area.%) until a limiting moment is reached, at 40 and 80 min for the technical and pilot plants, respectively. In batch or semi-batch processes, the reaction time is directly proportional to the amount of feed present, and the process takes more time in the pilot reactor but maintains some key aspects of the process. A comparison of the graph shown in Figure 10 with the temperature profile of the pilot plant (Figure 7) shows that after 80 min, more than 90% of the liquid phase was already collected in the separating drum at temperatures between 150 and 210 °C. It is interesting to note that, even though there was a change in the chemical composition of liquid fraction for all process scales (as expected in a semi-batch process), the average composition changed little between all process scales, slightly increasing for the laboratory (95.7%) when compared with the technical and pilot scales (93.7%), revealing that reaction

mechanism is not affected by the increase in process scale even if liquid yields are fairly different, as shown in Table 3, suggesting even further that a temperature gradient across the fixed bed (provoked by the increase in process scale) is responsible by the differences in product yields. As the reaction proceeds, the polymeric chain unzips, forming MMA until the condensation of products into polycyclic aromatic hydrocarbons and, subsequently, char occurs in higher temperatures [67]. With higher heating rates, the unzipping reaction of the polymer occurs until little to no char is formed, while in the case of larger fixed beds of feed, the outer part of the reactor reaches high temperatures, and the lower heating rates allow the formation of more char and gases, produced by the cracking of formed coal, producing aromatic hydrocarbons [84].

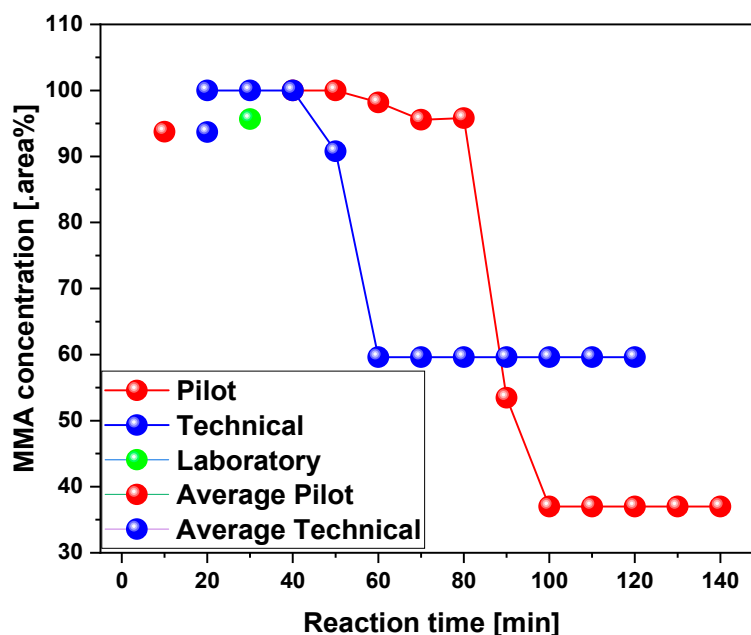


Figure 10. MMA concentration of the liquid phase of the three different production scales.

The formation of side products in the liquid fraction of the PMMAW depolymerization process is limited to a few substances, like methyl isobutyrate and aromatic hydrocarbons such as toluene, xylene, mesitylene and naphthalene. These aromatic compounds are formed in practically every pyrolysis process, being part of the mechanism of char formation [85], as explained before. Methyl isobutyrate is probably formed by the hydrogenation of MMA; during char formation, hydrogen is released and can be used for the hydrogenation of MMA to methyl isobutyrate. Figure 11 presents the variation in the chemical composition of minor compounds present in the liquid fraction of the technical scale. A similar behavior was observed in the pilot-scale reactor, and its chemical composition is presented in Figure 12.

It is possible to visualize the same trend in both production scales, with the liquid fraction composition mainly formed by MMA and later in the process changing to a more varied chemical composition reminiscent of the polymer chain cracking, with compounds such as methyl isobutyrate and EGDMA, as well as aromatic hydrocarbons produced by the cracking of char formed in the later stages of the pyrolysis process. The larger scale (pilot) also produced a non-identified heavy fraction, and it is not clear why it is not present in the liquid fraction formed on the technical scale. Due to the increased volume and mass flow on the pilot scale, the process takes longer, and fractioning liquid samples according to reaction time produces a more detailed version of the chemical composition variation of the samples as the feed changes. For the lower mass of the technical scale, the fractioning of samples every 10 min is not sufficient to obtain a detailed chemical composition, and some compounds could not be adequately detected, such as EGDMA and other aromatic

hydrocarbons, detected in the pilot-scale GC-MS spectra collected. The same could be said for the non-identified fraction: in the technical-scale GC-MS, they are probably present but could not be detected because they are present only in very small quantities, not showing appreciable concentration for detection in GC-MS. This is corroborated by the low mass fraction of the samples which showed the presence of NICs (90 and 100 min of reaction time), representing 6 and 2% of the recovered liquid, respectively.

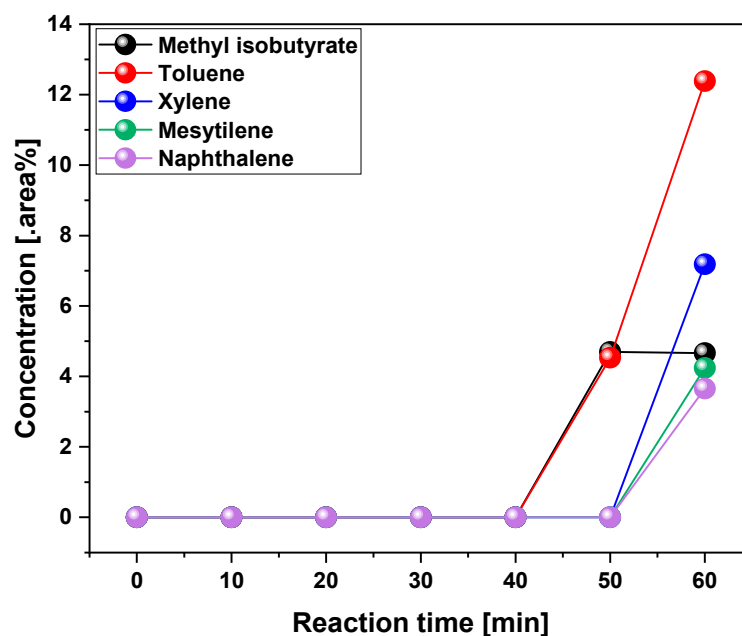


Figure 11. Concentration of side products of liquid fraction of PMMAW depolymerization on technical scale.

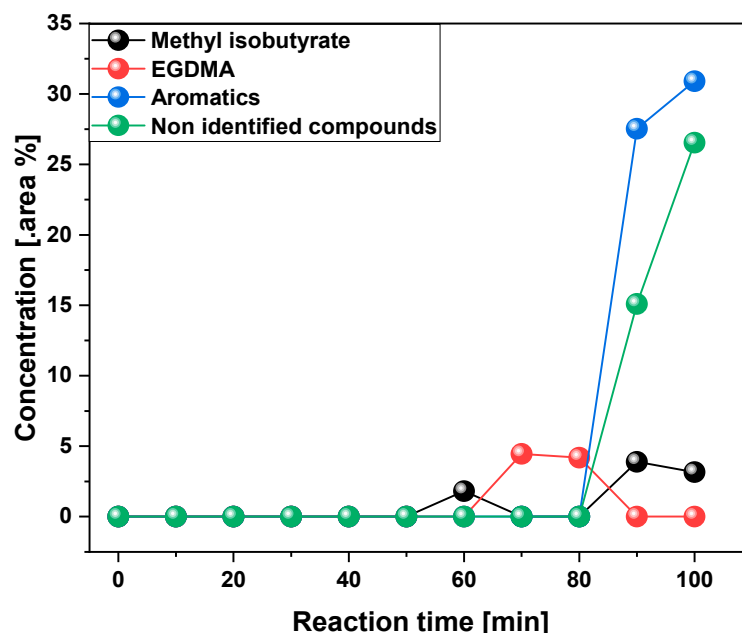


Figure 12. Concentration of side products of liquid fraction of PMMAW depolymerization on pilot scale.

The chemical composition variation of the liquid fraction of PMMAW depolymerization was further analyzed by conducting experiments on the technical scale at different

temperatures (Figure 13). The experiments conducted using 425 °C as a setpoint temperature allowed for obtaining a liquid fraction almost exclusively composed of MMA, whereas at higher temperatures, MMA concentration tends to decrease with increasing setpoint temperature. As explained earlier, in a semi-batch pyrolysis process, the reactor setpoint largely controls the extent of the reaction, and only a small difference separates one experiment from the other. It is important to remember that even with decaying MMA concentration, on average, the liquid fraction obtained during depolymerization presents a high MMA concentration (higher than 90%) for all temperatures. Different heating rates and different temperature gradients are observed though, especially for larger-sized reactors, such as the technical and pilot reactors, resulting in different product yields. For a temperature of 425 °C as a setpoint, this temperature gradient is minimized, resulting in a purified product and a higher amount of liquid. The reaction conducted at 425 °C resulted in a liquid fraction yield of 81%, compared to 61.7% and 61.3% for 450 and 475 °C, respectively, showing the effect of the minimization of this temperature gradient across the fixed heated zone of the reactor. A homogeneous temperature distribution is key in producing a liquid fraction with a high yield and chemical composition of MMA.

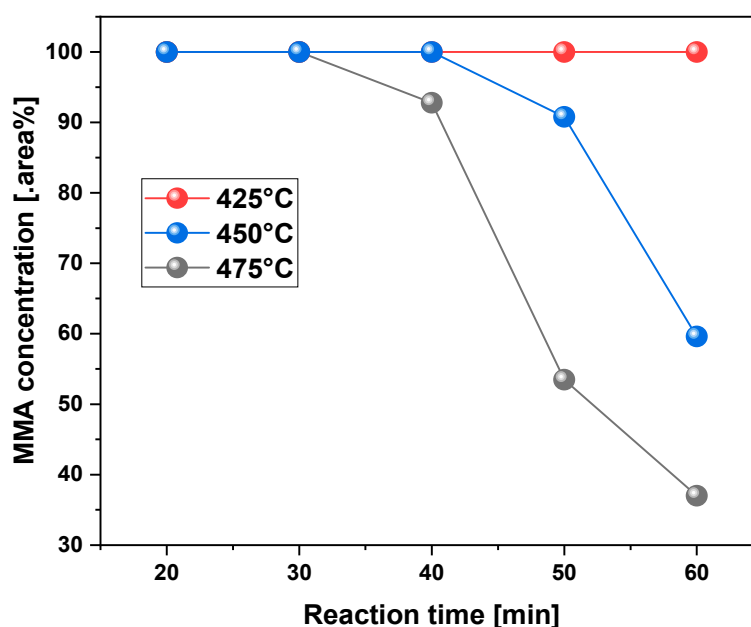


Figure 13. MMA concentration of liquid fraction of PMMAW depolymerization on technical scale.

4. Discussion

In a previous work, we detailed the PMMA depolymerization process from a perspective of the influence of temperature on the pilot scale [9]. Now, based on the differences found on smaller scales, we present detailed aspects of the three production scales of PMMAW depolymerization and highlight directions and choices in the process design of PMMA depolymerization in fixed bed semi-batch reactors. These types of reactors are among the simplest and cheapest choices, offering a great opportunity in the case of the PMMA recycling process because depolymerization achieves liquid yields higher than 80% with an MMA concentration of 90% [10–12,14,38,52]. As feedstock, we used waste PMMA from dental material.

First, the waste was characterized on the micro scale by TG and DSC analysis, and the thermal degradation curves (weight loss and DTG) were related to the possible mechanism of thermal degradation of PMMA. At low temperatures (200–300 °C), the reaction is initiated in the chain end and depropagates to the rest of the chain via a radical mechanism causing an unzipping of the polymer chain until termination by a bimolecular interaction. At higher temperatures (400–500 °C), the mechanism changes to a random scission-initiated

mechanism [67]. Even though it is possible to fit kinetic parameters considering more stages of decomposition [20,47], a single-step mechanism is capable of accurately describing the thermal decomposition of PMMAW, simplifying calculations and process design.

The heat flow involved in PMMAW decomposition was measured by DSC; it presents important parameters for the design of pyrolysis processes such as the heat of gasification and the amount of energy required to heat, depolymerize and vaporize the products of pyrolysis and could mean the approval or rejection of certain designs based on the economics of the MMA recovery process. The integration of the DSC curve produced values of -423 J/g for the decomposition peak and -1740 J/g for the heat of gasification. Even though it is an established tool for the analysis of chemical reactions of solid samples, including the calculation of parameters such as glass transition temperatures and heats of reaction, DSC has to be standardized for the analysis of pyrolysis processes due to some specifics. This technique presents great potential for the energetic analysis and process design of potential recycling processes using pyrolysis. Much of the variation in DSC analyses of pyrolysis processes arises from the following facts: there is a change in the weight of the sample during pyrolysis and variation in its heat capacity as volatiles flow out of the furnace and char is formed; a detailed mechanism of degradation must be known to accurately identify and measure heats of reaction of individual peaks; there are many ways to extract the heat capacity variation from the DSC curve as linear regression, fitting functions and others [71,81]. The heat of gasification measured (since it is based on an integral value) presents similarities with others in academic literature [81–83], while the peak of decomposition energy (-423 J/g) seems to only represent a part of the actual heat of decomposition of PMMAW, which should be at least represented by the sum of the heat of depolymerization (-578 J/g) and vaporization enthalpy of MMA (401 J/g). Nevertheless, DSC has been revealed to be an important tool in the investigation of the energy involved in pyrolysis processes, and we certainly will refine and use it for upcoming research since energy balances are rarely considered in process design papers.

The three production scales were analyzed from a material balance perspective by considering the reaction product yields and MMA concentration of the liquid phase, allowing the conclusion that there is a temperature gradient across the fixed bed of PMMAW in the semi-batch reactors that negatively influences both liquid yield and MMA concentration. This gradient seems to be larger in the case of thick beds such as those on the technical and pilot scales. We defined two variables called reactor load and power load, related to the ratio of the weight of feed to the available volume of the reactor and the ratio of the available power to the weight of feed, respectively. The results show that between the three process scales, both reactor and power loads decreased with an increase in process scale, the result of which is a decreased temperature of pyrolysis (200 – 300 °C) in the case of technical and pilot scales, while the laboratory scale produced results similar to the ones produced on the micro scale (TG), with degradation at higher temperatures such as 300 – 450 °C.

By comparison with established reaction mechanisms, it seems that the technical- and pilot-scale reactors tend to follow a mechanism initiated at the end-groups of the polymeric chain, with depropagation into MMA and termination via bimolecular interaction leading to an intermediate polymer that is transformed into char, as corroborated by higher char and gas yields (in this mechanism, there are radicals that distill out of the system and are probably in the gas phase). The presence of a temperature gradient makes depolymerization occur with lower temperatures in the center of the fixed bed reactor, favoring this mechanism. Furthermore, we identified that the temperature of 425 °C seems to favor MMA concentration in the liquid phase, as higher temperatures further increase the temperature gradient in the fixed bed due to the endothermic reactions occurring, favoring the formation of side products due to the simultaneous pyrolysis of the polymer intermediate present in the mechanism ($P + P$). For higher power loads, as in the case of the laboratory scale, the reaction proceeds via a random scission mechanism and depropagation to MMA until the end of the polymeric chain, and there is almost no influence of temperatures higher than 425 °C.

5. Conclusions

The presented work draws some conclusions about the PMMA depolymerization process regarding the scale-up of the fixed bed pyrolysis process and its analysis. Thermogravimetry coupled with differential scanning calorimetry is an interesting tool for assessing the potential of a feedstock for the production of fuels or chemical feedstock. The knowledge of reaction mechanisms and their association with TG/DTG peaks allows for needed calculations in process design, such as calculations of process economics, and also in assessing the best way to balance desired reaction pathways with the process mode and reactor.

DSC analysis shows the same potential as TG for the analysis of pyrolysis processes, as it evaluates the energy involved in the thermodynamic processes considered, but some standardization is still needed in order to effectively make it an indispensable tool in pyrolysis process design. With accurate knowledge of process thermodynamics, better reactors can be designed, with optimized yields and higher efficiency.

To be able to analyze the process on different scales, we created two variables, namely reactor load (kg/L) and power load (W/kg), relating process parameters to the geometry of the reactor and heating transfer rate, and they can adequately describe what is presented in the scale-up, illustrating critical differences between the three process scales analyzed. This evaluation showed that low power loads lead to increased temperature gradients and that the reaction proceeds until termination by bimolecular interaction, reducing liquid yields and increasing the formation of side products. This could be used in the operation of large vessels or when one needs to make changes to specified batch weights. Further study of the power load concept could also be performed to create optimized control systems for pyrolysis, improving process yields.

Supplementary Materials: The following supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/en17051196/s1>: Table S1. Class of compounds, sum of peak areas, chemistry registry numbers (CAS) and retention times of molecules identified by gas chromatography–mass spectrometry (GC-MS) in the liquid phase for depolymerization of PMMA-based dental resin fragments/residues at 425 °C, atmospheric pressure and reaction times of 20, 30, 40, 50 and 60 min, on the technical scale. Table S2. Class of compounds, sum of peak areas, chemistry registry numbers (CAS) and retention times of molecules identified by gas chromatography–mass spectrometry (GC-MS) in the liquid phase for depolymerization of PMMA-based dental resin fragments/residues at 450 °C, atmospheric pressure and reaction times of 30, 40, 50 and 60 min, on the technical scale. Table S3. Class of compounds, sum of peak areas, chemistry registry numbers (CAS) and retention times of molecules identified by gas chromatography–mass spectrometry (GC-MS) in the liquid phase for depolymerization of PMMA-based dental resin fragments/residues at 475 °C, atmospheric pressure and reaction times of 20, 30, 40, 50 and 60 min, on the technical scale. Table S4. Class of compounds, sum of peak areas, chemistry registry numbers (CAS) and retention times of molecules identified by gas chromatography–mass spectrometry (GC-MS) in the liquid phase for depolymerization of PMMA-based dental resin fragments/residues at 450 °C, atmospheric pressure and reaction times of 40, 50, 60, 70, 80, 90 and 100 min, on the pilot scale. Table S5. Process conditions and programming of Chromatographic tests.

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